Calculating EPR properties: accounting for molecular environment and temperature in DFT

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In the last decade, ab-initio computational methods are increasingly used to complement experiments. Density Functional Theory (DFT) is particularly popular since it allows relatively fast calculations on fairly large molecular systems. Theoretical developments have also made it possible to calculate magnetic resonance properties of paramagnetic systems within the DFT framework – for instance hyperfine coupling tensors and g tensors of radicals. Such calculations constitute an additional tool for spectral interpretation and identification of radical structures.

But quite regularly, only a small part of the molecular system (e.g. the paramagnetic center) is considered in the DFT calculations. This approach is straightforward and computationally attractive but neglects intermediate- and long range intermolecular effects typical for the medium. Yet, the **molecular environment** of a paramagnetic center – e.g. a crystal or solution phase – can have an impact, both on the calculated geometry and EPR properties. Incorporating it explicitly can therefore significantly improve the description of the system. One way to efficiently take the molecular environment into account is by performing DFT calculations in a periodic approach, in which the structure inside a simulation cell is subject to periodic boundary conditions. In this way, simulations are performed on an infinitely extended, periodically repeated structure. This method is ideally suited to study crystals, but it is also computationally attractive for the simulation of (paramagnetic) compounds in a solution phase.

Another factor that is usually not accounted for in DFT simulations is **temperature**. A real molecular structure is subject to thermal vibrations, which in turn affect the magnetic resonance parameters. However, a *static* approach is often adopted in calculations: the structural and EPR properties are only determined for a conformation corresponding to a (local) minimum of the potential energy surface (formally at 0 K). This is usually sufficient, but is quite approximate when a molecular system is able to sample various conformations on the potential energy surface. In that case, it is desirable to explicitly account for temperature effects by performing *molecular dynamics* simulations, in which the time-evolution of a molecular system and the interactions within it are numerically evaluated over a period of time. Temperature-dependent magnetic resonance parameters can then be obtained by calculating them at regular intervals during the time evolution and averaging.

In this talk, the importance of these effects on calculated magnetic resonance properties will be illustrated for two types of systems: (i) **radiation-induced radicals in sugar crystals**, which can be considered as model systems to gain a more fundamental understanding of the action of ionizing radiation to biomolecules, (ii) intermediate **radical states of the cofactor in a flavin-containing protein**, which play an active role in the redox properties of various enzymes.